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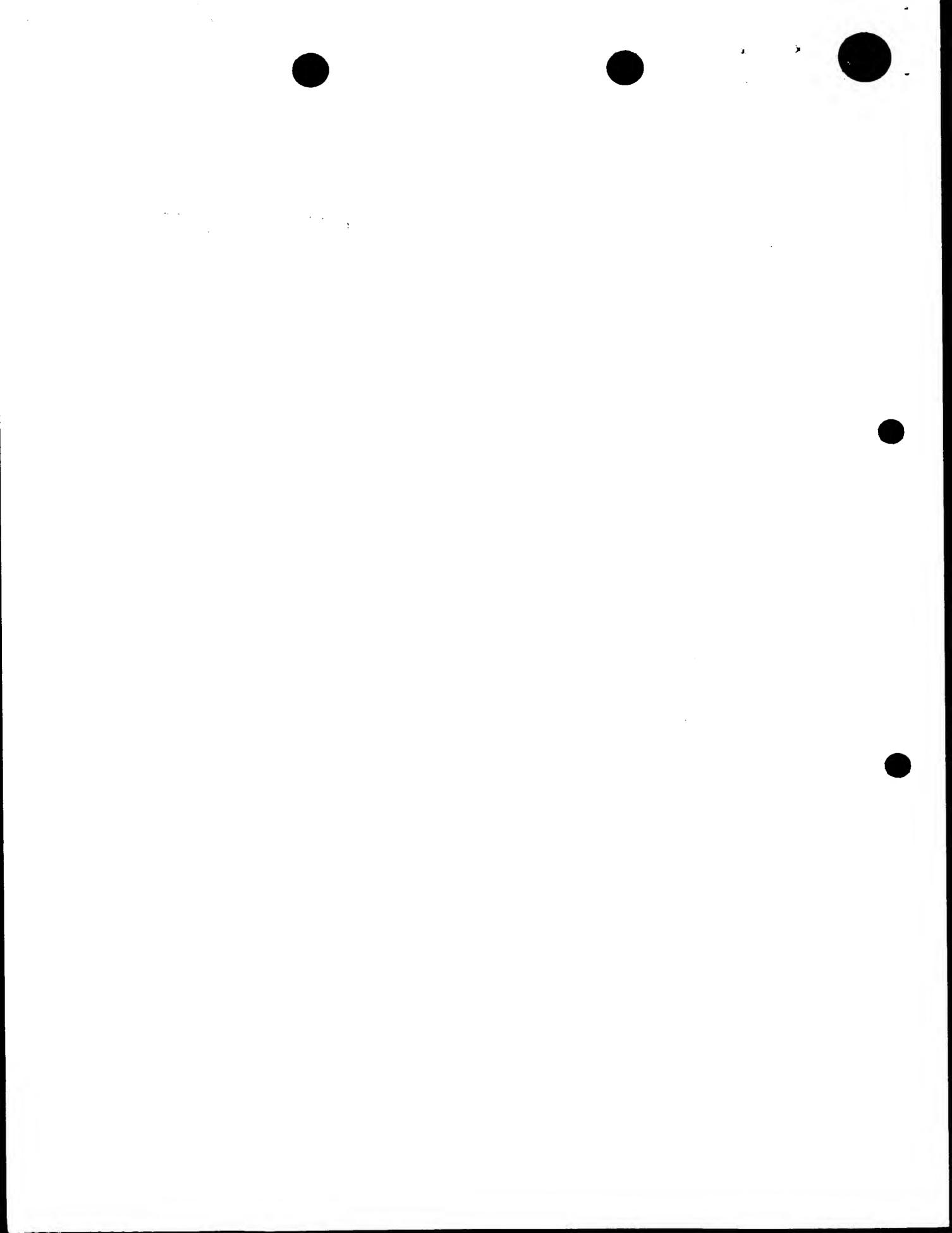
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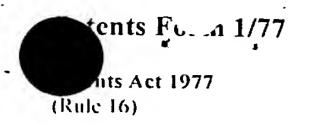
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Liquid Crystal Device

5. Name of your agent (if you have one)

Patents ADP number (if you know it)

J B Edwards

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PATENT APPLICATION LIQUID CRYSTAL DEVICE

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Slippery Surfaces cases:

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- 1 (P2618) general case genslip.1 cover all the following file on same day
- 2 (P2619) bistable case bislip1.doc was pat4 etc involves HP
- 3. (P2620) twisted nematic taslip1.doc improves TN devices was pat5 etc
- 4 (P2621) ferro electric feslip1.doc improves FELCDs

LIQUID CRYSTAL DEVICE

This invention relates to the alignment and switching of nematic liquid crystal devices.

Liquid crystal devices typically comprise of a thin layer of a liquid crystal material contained between cell walls. Optically transparent electrode structures on the walls allow an electric field to be applied across the layer causing a re-ordering of the liquid crystal molecules.

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There are three known types of liquid crystal material nematic, cholesteric and smectic each having different molecular ordering. The present invention concerns devices using nematic and long pitch cholesteric materials.

In order to provide displays with a large number of addressable elements it is common to make the electrodes as a series of row electrodes on one wall and a series of column electrodes on the other cell wall. These form e.g. an x,y matrix of addressable elements or pixels and for twisted nematic types of device are commonly addressed using rms addressing methods.

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Twisted nematic (TN) and phase change devices are switched to an ON state by application of a suitable voltage and allowed to switch to an OFF state when the applied voltage falls below a lower voltage level, i.e. these devices are monostable. For a twisted nematic type of device (90° or 270° twist as in US 4.596,446) the number of elements that can be rms addressed is limited by the steepness of a device transmission verses voltage curve (as described by Alt and Pleschko in IEEE Trans ED vol ED 21, (1974) P.146 - 155). One way of improving the number of pixels is to incorporate thin film transistors adjacent to each pixel; such displays are termed active matrix displays.

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An advantage of nematic types of devices is the relatively low voltage requirements. They are also mechanically stable and have a wide temperature operating range. This allows construction of small and portable battery powered displays. An alternative twisted nematic device is one which is switched from a non-twisted state at zero volts to a twisted state at a higher voltage as described in GB 9607854.8 which will be referred to in this patent as a VCT device.

One problem with the twisted nematic device is that the contrast ratio of a normally white display remains at a low value until the voltage is increased to a value considerably higher than the threshold voltage. This is due to the nematic material close to the cell walls which does not fully reorient in the applied field due to the strong zenithal anchoring imposed by the surface alignment layer. This lack of surface reorientation also leads to higher voltage operation in the VCT device.

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The terms azimuth or azimuthal is used herein to define the molecular (or director n) alignment angle movement or energy in the plane of the wall surface. The terms zenith or zenithal is used herein to define the molecular alignment angle movement or energy in a plane normal to the wall surface

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According to this invention, the contrast ratio of a twisted nematic device can be improved by using an additional surface treatment which reduces the zenithal anchoring energy of the surface and thereby allows field-induced reorientation of the near-surface nematic layers. Such a treatment also has the added advantage of leading to a lowering of the threshold voltage. Lower voltage operation is preferable for both passive matrix and active matrix twisted nematic devices as it allows a display to operate with a lower power consumption.

According to this invention a twisted nematic liquid crystal device capable of being switched from a twisted stated to a non twisted state comprises:

5 two cell walls enclosing a layer of nematic liquid crystal material:

electrode structures on both walls for applying an electric field across the liquid crystal layer:

a surface alignment on both cell walls providing alignment direction to liquid crystal molecules and arranged so that a twisted nematic structure is formed across the liquid crystal layer at either zero volts or at a higher voltage:

means for distinguishing between the two different optical states of the liquid crystal material;

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means for reducing zenithal anchoring energy in the surface alignment on one or both cell walls.

Additionally the azimuthal anchoring energy may also be reduced.

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The means for reducing azimuthal anchoring energy and zenithal anchoring energy may be an oligomer containing esters, thiol, and/or acrylate monomers either spread on the surface or added to the liquid crystal material, e.g. the materials N65 and MXM035.

The oligomers may migrate preferentially to the surface in order to minimise the surface free energy. This may dilute the amount of liquid crystal at the surface leading to an effective reduction in the order parameter, S which is defined by (P. G. deGennes, The Physics of Liquid Crystals, Clarandon Press, Oxford 1974):

$$S = \frac{1}{2} \left\langle \left(3\cos^2 \theta - 1 \right) \right\rangle$$

The order parameter is an indication of how well molecules align in a cell.

Additionally the phase of the liquid crystal material at the surface may be changed by the oligomers, eg from nematic or long pitch cholesteric to isotropic.

The treatment may be used in conjunction with a surface which induces monostable pretilted nematic alignment.

The alignment layer may be a rubbed polymer surface as described in S. Ishihara et al, Liq. Cryst., vol.4, no. 6, p.669-675 (1989) or an obliquely evaporated inorganic material as described in W. Urbach, M. Boix and E. Guyon, Appl. Phys. Lett., vol. 25, no. 9, 479 (1974) or a polymer surface where in-plane anisotropy is achieved by illumination with polarised light such as M. Schadt et al, Jpn. J. Appl. Phys., v. 31, no.7, p. 2155 (1992).

Alternatively the alignment layer may be a surface monograting with an asymmetric groove profile as described in G. P. Bryan-Brown and M. J. Towler. "Liquid crystal device alignment". GB 2.286.466A (GB9402492.4).

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The alignment directions on the two surface may be substantially perpendicular.

The nematic liquid crystal may contain a small amount (<5%) of a chiral dopant material e.g., R1011, CB15 Merck.

The cell walls may be substantially rigid e.g. glass material, or flexible e.g. polyolefin.

The electrodes may be formed as a series of row and column electrodes arranged and an x,y matrix of addressable elements or display pixels. Typically the electrodes are $200\mu m$ wide spaced $20\mu m$ apart.

Alternatively, the electrodes may be arranged in other display formats e.g. $r-\theta$ matrix or 7 or 8 bar displays.

The invention will now be described, by way of example only with reference to the accompanying drawings of which:

Figure 1 is a plan view of a matrix multiplexed addressed liquid crystal display:

Figure 2 is the cross section of the display of figure 1;

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Figure 3 shows the theoretical surface director tilt versus voltage for values of surface extrapolation lengths L.

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Figure 5 shows the configuration for photolithographic exposure leading to the formation of an asymmetric monograting.

- 6 -Figure 6 shows the transmission versus voltage data for two cells, one of which (dotted line) has been treated with an additive (Norland 65) to give weak anchoring. Gratings have been used on both surfaces for alignment. Figure 7 shows the optical contrast ratio versus voltage data for two cells. one of 5 which (dotted line) has been treated with an additive to give weak anchoring. Figure 8 shows the transmission versus voltage data for two cells, one of which (dotted line) has been treated with an additive (MXM035) to give weak anchoring. Gratings have been used on both surfaces for alignment. Cell gaps are $2.05\mu m$ 10 Figure 9 shows the transmission versus voltage data for two cells, one of which (dotted line) has been treated with an additive (MXM035) to give weak anchoring. Gratings have been used on both surfaces for alignment. Cell gaps are 4.6µm. 15 Figure 10 shows the transmission versus voltage data for two cells, one of which (dotted line) has been treated with an additive (MXM035) to give weak anchoring. Rubbed polymer layers have been used on both surfaces for alignment. Cell gaps are 4.6µm. 20 Figure 11 shows the transmission versus voltage data for two VCT cells, one of which (dotted line) has been treated with an additive (MXM035) to give weak anchoring energy. The display in figures 1, 2 comprises a liquid crystal cell 1 formed by a layer 2 of 25 nematic or long pitch cholesteric liquid crystal material contained between glass walls 3. 4. A spacer ring 5 maintains the walls typically 2-10 m apart. Additionally numerous beads of the same dimensions may be dispersed within the liquid crystal to maintain an accurate wall spacing. Strip like row electrodes 6 e.g. of SnO2 or ITO are formed on one wall 3 and similar column electrodes 7 are formed on the other wall 4. 30 With m-row and n-column electrodes this forms an m×n matrix of addressable

elements or pixels. Each pixel is formed by the intersection of a row and column electrode. A row driver 8 supplies voltage to each row electrode 6. Similarly a column driver 9 supplies voltages to each column electrode 7. Control of applied voltages is from a control logic 10 which receives power from a voltage source 11 and timing from a clock 12.

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Either side of the cell 1 are polarisers 13, 13' arranged with their polarisation axis substantially crossed with respect to one another. An additional optical compensator such as a stretched plastic film may also be added between the liquid crystal cell and one of the polarisers. A partly reflecting mirror 16 may be arranged behind the cell 1 together with a light source 15. These allow the display to be seen in reflection and lit from behind in dull ambient lighting. For a transmission device, the mirror may be omitted.

- Prior to assembly, the cell walls 3, 4 are treated with alignment treatments to provide a monostable pretilted alignment. Finally the cell is filled with a nematic material which may be e.g. E7, ZLI2293 or MLC 6608 (Merck), and may include a chiral additive such as CB15 or R1011 (Merck).
- These materials may contain the treatment or a precursor of the treatment which leads to a lowering of the anchoring energy.

In general anchoring of a nematic liquid crystal on a surface can be described by three macroscopic parameters, pretilt, zenithal anchoring energy and azimuthal anchoring energy. Consider a surface in the x-y plane, parallel to the cell walls. The pretilt (θ_p) is defined as the preferred angle of inclination of the nematic director with respect to the x-y plane. To change the tilt of the surface director from θ_p to an arbitrary tilt θ , an energy per unit area of W must be supplied to the system where [A. Rapini and M. Papoular, J. Phys. (Paris), 36, C-1, 194 (1975)]:

$$W = W_{\theta} \sin^2 \left(\theta - \theta_{p} \right) \tag{1}$$

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 W_{θ} is the zenithal anchoring energy and represents the energy required in order change the tilt of the surface director by 90°. If the director has a preferred in-plane orientation, say along the x axis, then an energy must be supplied to the system to change this orientation. The energy is now given by

$$W = W_{\phi} \sin^2 \phi \tag{2}$$

where ϕ is the change in the in-plane orientation and W_{ϕ} is the azimuthal anchoring energy.

Pretilt and zenithal anchoring can be achieved from most solid surfaces while azimuthal anchoring usually requires some extra treatment in order to obtain a preferred in-plane direction such as an anisotropic polymer, obliquely evaporated film or a surface grating. For most surfaces W_{θ} and W_{ϕ} are large and so reorientation of the director at the surface only occurs at high voltages.

The effect of the weak zenithal anchoring on a twisted nematic device is discussed below.

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The improvement in operation of a 90° twisted nematic cell with weak surface anchoring was first analysed theoretically. The static configuration of the cell was calculated by minimising the total free energy which is dictated by the Eular-Lagrange equation in the bulk and by equations (1) and (2) at the surfaces. The zenithal anchoring energy W_{θ} was then relaxed from its usual large value and the effect on the static configuration was calculated. Figure 3 shows several curves calculated for different surface extrapolation lengths. L where $L = k_{11} / W_{\theta} \cdot d$. The parameters common to all the curves are ;

 $k_{22}/k_{11} = 0.6$; $k_{33}/k_{11} = 1.5$; $\epsilon_{para} = 14.0$; $\epsilon_{per} = 4.0$; Cell twist = 90°; Surface pretilt = 5°

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The reduced voltage is defined as the voltage which has been normalised by the

Frederiskz threshold voltage (= $\sqrt{k_{11}/\epsilon_o}\Delta\epsilon$). Figure 3 shows the surface tilt angle as a function of applied voltage. For infinite zenithal anchoring energy (L=0.0) the tilt remains fixed at the zero volt pretilt value. However for finite anchoring (L>0) all the curves show that the surface director is reoriented by the applied field and shows an increasing tilt angle with voltage. It is expected that this voltage induced tilt will lead to a better contrast ratio in a typical normally-white twisted nematic device.

Figure 4 has been calculated with the same parameters as figure 3 but now shows the voltage dependent tilt in the middle of the nematic layer. This tilt angle is the dominant parameter in dictating the optical transmission of the twisted nematic device. Therefore it is clear to see that a surface offering a finite L will lead to a lower voltage, steeper electrooptic response.

Therefore the above modelling has shown that a surface treatment which lowers W_{θ} will lead to a twisted nematic device which has a lower voltage threshold, a steeper electrooptic response and a higher contrast at a given voltage

Example 1

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An example of a weak anchoring treatment applied to a twisted nematic is now given. The pretilted alignment surface used in this example was an asymmetric monograting as described in GB 9402492.4; GB-A-2.296.466: WO-95/22078.

The treatment consists of adding a small (1-10%) amount of a UV curing adhesive material to the nematic prior to cell filling. Examples of suitable materials include N65. N63. N60 or N123 (All manufactured by Norland Products Incorporated, North Brunswick, NJ, USA). In this particular example, one of these materials (N65) is used as an additive to the nematic E7 (Merck). This material contains a mixture of esters and acrylate monomers which polymerise under UV radiation.

Before using the N65 additive in a twisted nematic device a set of experiments were carried out in order to show the effect of the N65 treatment on the zenithal anchoring energy, W_{θ} . This quantity can be calculated by measuring the saturation voltage, V_{s} . That is, the voltage at which the director tilt in the cell is perpendicular to the surface throughout the thickness of the cell. This can be measured in cells where the surfaces have no preferred alignment direction. In this case flat surfaces of hardbaked photoresist were used (Shipley 1805). This material was spin coated on ITO coated glass to form a 0.55 μ m thick layer. Baking at 160°C for 45 minutes ensured full insolubility in the liquid crystal. When filled with N65/E7 mixtures, these cells show a random Schlerien texture. The saturation voltage was measured by observing when the transmitted intensity of the Schlerien texture falls to zero when viewed between crossed polarisers. W_{θ} is then given by

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$$W_{\theta} \approx \frac{3.85\sqrt{\varepsilon_0 \Delta\varepsilon k_{11}} \cdot V_s}{d} \tag{4}$$

where d is the liquid crystal thickness, k_{11} is the liquid crystal splay elastic constant and $\Delta\epsilon$ is the liquid crystal permittivity anisotropy.

Results are shown in table 1. The pure E7 cell failed to show a black state before cell breakdown and so only a lower limit on W_{θ} can be given. In the cases of the E7 containing N65, the curing was performed in a fused silica cell for 10 minutes prior to transferring the mixture to a separate measurement cell. The exposure was carried out using an unfiltered mercury lamp with an optical output of 2.0mW/cm² at a raised temperature of 65°C.

Cell mixture	W _θ (N m ⁻¹)
Pure E7	>5×10 ⁻²
2% N65 in E7	6.3×10 ⁻³

Table 1

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Surface zenithal anchoring energies modified by the presence of N65. 10

The above results clearly show that the N65 has reduced the value of W_{θ} in a cell with flat surfaces. The next step is to study the effect of this additive on the operation of a twisted nematic device.

Such a twisted nematic device may employ asymmetric monogratings to induce pretilted alignment and be fabricated in the following way as shown in Figure 5:

UV exposure to preharden the photoresist (3.36 J/cm² at 254nm).

Shipley 1805 photoresist 20 was spin coated at 3000 rpm onto ITO coated glass 21 for 30 seconds. Next the photoresist layer 20 was baked at 90°C for 30 minutes to remove the solvent. Exposure of the photoresist through a mask 22 was carried out using off axis hard contact photolithography. The mask 22 consisted of a chrome on glass pattern with a pitch of 1μm (0.5μm gaps and 0.5μm chrome strips). The exposure time was set to 540 seconds with an incident power of 0.15 mW/cm² from a mercury lamp. Development was then carried out in Shipley MF319 for 10 s followed by a water rinse. Samples were finally baked at 160°C for 45 minutes after first receiving a deep

The above process resulted in a surface monograting with a 1μm pitch and a 0.5μm peak to trough groove depth. The profile is asymmetric (approximately sawtooth in form) which leads to a pretilted alignment if the nematic is under the influence of a bulk twist torque (see GB-A-2.296.466: WO-95/22078). These surfaces were constructed into cells in which the groove direction on one surface was orthogonal to the groove direction on the other. The cell gap was set to 2.05μm which corresponds to the first Gooch and Tarry minimum when used with E7 (J. Phys. D. Appl. Phys. vol. 8, p. 1575 (1975)). Filling was then carried out using E7 in the isotropic phase (65°C) followed by slow cooling to room temperature.

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The electrooptic response of cells containing different N65/E7 mixtures was then recorded by placing the twisted nematic cell between crossed polarisers which were oriented parallel to the adjacent grating alignment directions. Transmission was measured using a photodiode with a photo-optic response during the application of a 1kHz sinusoidal drive waveform. Figure 6 shows the transmission versus rms voltage for two cells one of which was treated to give weak anchoring. The weak anchoring treatment consisted of adding 2% N65 to E7 and curing for 10 minutes in a pre-cell before transferring the material to the test cell. The data clearly shows that the weak anchoring treatment has lowered the operating voltage. A transmission of 50% of the zero volt value is reached at a voltage of 1.83 V for the weak anchored surface and 2.13 V for the strong anchored surface. The power consumption of a display can be considered in the most simple case as the power required to charge and discharge a capacitor which is proportional to V². Therefore the weak anchored surface is expected to allow a power saving of roughly 35%.

The second improvement of the weak anchored cell is the improved optical contrast ratio as shown in figure 7. At 5 V the weak anchored cell has a contrast ratio of 126 while the strong anchored cell has a contrast ratio of 49. At 8 V the difference is even larger (410 and 74 respectively). Therefore if a particular application demands a certain contrast ratio then it can be reached at a much lower voltage with a weak

anchored surface. The weak anchoring has also lead to a slight increase in the steepness of the electrooptic response. For the weak anchored surface V_{90} - V_{50} is 0.454 V while for the strong surface this quantity is 0.510 V: V_{90} and V_{50} being the voltage at transmissions of 90% and 50% of the zero voltage transmission value respectively.

In summary the above experimental results have shown qualitative agreement with the theoretical analysis by demonstrating that a surface which has been treated to give a lower W_{θ} can improve a twisted nematic device. The improvements include a lower voltage threshold, a steeper electro optic response and a higher optical contrast.

Example 2

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In this example MXM035 (Merck) was used as the weak anchoring treatment. The alignment surfaces were asymmetric monogratings as described in example 1.

The MXM035 consists of two parts which were mixed in equal quantities. This mixture was then added to E7 nematic to give a 4% solution which was cured in a fused silica cell (as described in example 1) before transferring to a test cell. A measurement of W_{θ} for the 4% solution revealed a value of $3.85\times10^{-4} J/m^2$. This is 16 times smaller than the value of measured for N65 (in example 1). Therefore the MXM 035 treatment is expected to have a larger effect on the operating behaviour of a TN device.

Cells were constructed using asymmetric monogratings as alignment surfaces. The groove direction on one surface was orthogonal to that on the other to ensure a twisted configuration with a liquid crystal twist of roughly 90°. The cell gap was set to 2.05μm (the first Gooch and Tarry minimum). Figure 8 shows the transmission versus rms voltage for two cells, one of which was treated with 4% MXM035 to give weak anchoring. In this case the weak anchoring treatment has lead to a very large decrease

in operating voltage. A transmission of 50% of the zero volt value is reached at a voltage of 0.8 V for the weak anchored surface compared to 1.93 V for the strong anchored surface. Hence the weak anchored TN is expected to use only 17% of the operating power of a conventional TN.

Weak anchoring treatments can also lead to improvements in performance when the cell gap is larger. To demonstrate this, data was taken from two more TN cells which had been constructed with a cell gap of 4.6 μ m which corresponds to the second Gooch and Tarry minimum for E7. One of these was filled with pure E7 while the other was filled with 4% MXM035 in E7 which had been precured as described above. Figure 9 shows the electrooptic response for these two cells. Once again the weak anchored cell shows a response at a much lower voltage. The 50% transmission occurs at 1.07 V for the weak anchored TN compared to 2.16 V for the conventional TN. The weak anchoring treatments are expected to change the dynamic response of the TN and so optical response times were measured for these cells for switching between 0 V and 4V as shown in table 2. It can be seen that the addition of MXM035 has lead to a decrease in switch-on time (τ_{on}) and an increase in switch-off time (τ_{on}). This behaviour is consistent with weak surface anchoring.

Cell Mixture	τ _{on} (ms)	τ _{offee} (ms)
E7	6.8	15.5
E7 + 4%MXM035	2.5	24.0

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0-4 V optical switching times for second minimum TN cells with strong or weak anchoring. .

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Example 3

Weak anchoring treatments can also be used in conjunction with other surface alignments to improve TN performance. In this example the MXM035 treatment is used in conjunction with a rubbed polymer alignment.

Rubbed alignment surfaces were prepared by spin coating a layer of probomide 32 (Ciba Geigy) onto ITO coated glass and baking the substrates at 300°C. The surfaces were then rubbed in one direction by a nylon cloth attached to a rotating roller. Finally cells were constructed in which the rubbing direction on one surface was orthogonal to that on the other. The cell gap was set to 4.6µm using monodispersed spacer beads in the edge seal. Figure 10 shows a comparison of electrooptic responses recorded from two TN cells, one filled with E7 and the other filled with E7+ 4% MXM035. Once again the addition of the weak anchoring treatment has lead to a reduction in operating voltage.

Example 4

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One particular type of twisted nematic device is the VCT device which switches from a substantially non-twisted state to a twisted state when a voltage is applied. In this example the operation of the VCT device is improved by the addition of a weak anchoring treatment. The surface alignment in this example was provided by asymmetric grating surfaces as described in example 1.

The weak anchoring treatment was MXM035 mixed from 10 % of part A and 90% of part B. 4% of this mixture was added to nematic MLC 6608 which has a negative dielectric anisotropy. The MXM035 was then cured by placing the MXM035/MLC6608 mixture in a glass cell and exposing to UV radiation (10 minutes at 2.0mW/cm² while at a temperature of 65°C). After curing the mixture was used to fill a VCT test cell.

The VCT cells were constructed so that the grating grooves on one surface were orthogonal to those on the other. Prior to construction the grating on one surface was treated with a chrome complex surfactant in order to induce a homeotropic boundary condition (molecules perpendicular to the wall surface). The grating on the other surface was left untreated in order to induce a planar boundary condition. The cell gap was set to 5.3µm using spacer beads in the edge seal. Figure 11 shows the electrooptic response of two VCT devices, one of which contains the weak anchoring treatment. The VCT containing pure MLC6608 exhibits 50% transmission at a voltage of 2.91 V while the VCT containing 4% MXM035 in MLC 6608 exhibits 50% transmission at a voltage of 1.52 V: Therefore the weak anchoring treatment has lead to a dramatic decrease in operating voltage.

The dynamic response times of the VCT were measured for these cells for switching between 0 V and 5V as shown in table 3. It can be seen that the addition of MXM035 has lead to a decrease in switch-on time (τ_{on}) and an increase in switch-off time (τ_{off}) .

Cell Mixture	τ _{on} (ms)	τ _{offee} (ms)
MSc 6608	86	60
MSC 6608 +	60	112
4%MXM035		

Table 3

20 0-5 V optical switching times for VCT cells with strong or weak anchoring.

The above examples show that the addition of oligomeric materials (Norland 65, MXM035) into cells with either grating surfaces or rubbed polymer surfaces will lead to a reduction in the operating voltage of a twisted nematic device.

The monomer materials used may include the following, which are given only by way of example:

methyl acrylate

ethyl acrylate

propyl acrylate

butyl acrylate

pentyl acrylate

2-methylbutyl acrylate

hexyl acrylate

heptyl acrylate

octyl acrylate

nonyl acrylate

decyl acrylate

ethyl hexyl acrylate

methyl methacrylate

ethyl methacrylate

propyl methacrylate

butyl methacrylate

pentyl methacrylate

2-methylbutyl methacrylate

hexyl methacrylate

heptyl methacrylate

octyl methacrylate

nonyl methacrylate

decyl methacrylate

ethyl hexyl methacrylate

styrene

ethylene glycol diacrylate

1.2-propylene glycol diacrylate

propane-1.3-diol diacrylate

butane-1.4-diol diacrylate

pentane-1,5-diol diacrylate

hexane-1,6-diol diacrylate

heptane-1,7-diol diacrylate

octane-1,8-diol diacrylate

nonane-1,9-diol diacrylate

decane-1,10-diol diacrylate

glycerol triacrylate

trimethylolpropane triacrylate

pentaerythritol triacrylate

pentaerythritol tetraacrylate

di-pentaerythritol hexaacrylate

ethylene glycol dimethacrylate

1,2-propylene glycol dimethacrylate

propane-1.3-diol dimethacrylate

butane-1.4-diol dimethacrylate

pentane-1.5-diol dimethacrylate

hexane-1,6-diol dimethacrylate

heptane-1,7-diol dimethacrylate

octane-1.8-diol dimethacrylate

nonane-1,9-diol dimethacrylate

decane-1.10-diol dimethacrylate

glycerol trimethacrylate

trimethylolpropane trimethacrylate

pentaerythritol trimethacrylate

pentaerythritol tetramethacrylate

di-pentaerythritol hexamethacrylate

A further class of polymers includes di-thiol/diene polymers prepared by the copolymerisation of difunctional alkenes with difunctional thiols under free radical conditions. Monofunctional and/or polyfunctional alkenes and/or thiols may be incorporated in order to modify the properties of the polymer, for example to reduce the molecular weight of the polymer or to introduce a controlled degree of crosslinking in the polymer. The following materials given by way of example only may be included in polymers suitable for the subject of the invention:

methyl acrylate ethyl acrylate propyl acrylate butyl acrylate pentyl acrylate 2-methylbutyl acrylate hexyl acrylate heptyl acrylate octyl acrylate nonyl acrylate decyl acrylate ethyl hexyl acrylate methyl methacrylate ethyl methacrylate propyl methacrylate butyl methacrylate pentyl methacrylate 2-methylbutyl methacrylate hexyl methacrylate heptyl methacrylate octyl methacrylate nonyl methacrylate decyl methacrylate

styrene ethylene glycol diacrylate 1.2-propylene glycol diacrylate propane-1,3-diol diacrylate butane-1,4-diol diacrylate pentane-1.5-diol diacrylate hexane-1,6-diol diacrylate heptane-1,7-diol diacrylate octane-1,8-diol diacrylate nonane-1,9-diol diacrylate decane-1,10-diol diacrylate glycerol triacrylate trimethylolpropane triacrylate pentaerythritol triacrylate pentaerythritol tetraacrylate di-pentaerythritol hexaacrylate ethylene glycol dimethacrylate 1.2-propylene glycol dimethacrylate propane-1.3-diol dimethacrylate butane-1,4-diol dimethacrylate pentane-1.5-diol dimethacrylate hexane-1.6-diol dimethacrylate

heptane-1,7-diol dimethacrylate

ethyl hexyl methacrylate ethylene glycol divinyl ether 1.2-propylene glycol divinyl ether propane-1,3-diol divinyl ether butane-1,4-diol divinyl ether pentane-1.5-diol divinyl ether hexane-1.6-diol divinyl ether heptane-1.7-diol divinyl ether octane-1,8-diol divinyl ether nonane-1,9-diol divinyl ether decane-1,10-diol divinyl ether glycerol trivinyl ether trimethylolpropane trivinyl ether divinyl benzene butane-1,3-diene pentane-1,4-diene hexane-1,5-diene heptane-1.7-diene octane-1.7-diene nonane-1,8-diene decane-1,9-diene ethylene glycol dithioglycollate 1.2-propylene glycol dithioglycollate propane-1.3-diol dithioglycollate butane-1.4-diol dithioglycollate pentane-1,5-diol dithioglycollate hexane-1.6-diol dithioglycollate heptane-1.7-diol dithioglycollate octane-1.8-diol dithioglycollate nonane-1.9-diol dithioglycollate decane-1.10-diol dithioglycollate

octane-1.8-diol dimethacrylate nonane-1.9-diol dimethacrylate decane-1.10-diol dimethacrylate glycerol trimethacrylate trimethylolpropane trimethacrylate pentaerythritol trimethacrylate pentaerythritol tetramethacrylate di-pentaerythritol hexamethacrylate ethylene glycol diallyl ether 1.2-propylene glycol diallyl ether propane-1.3-diol diallyl ether butane-1,4-diol diallyl ether pentane-1.5-diol diallyl ether hexane-1.6-diol diallyl ether heptane-1,7-diol diallyl ether octane-1,8-diol diallyl ether nonane-1.9-diol diallyl ether decane-1,10-diol diallyl ether glycerol triallyl ether trimethylolpropane triallyl ether di-allyl malonate di-allyl succinate di-allyl glutanate di-allyl hexane-1,6-dicarboxylate di-allyl keptane-1.7- dicarboxylate di-allyl octane-1.8- dicarboxylate di-allyl nonane-1.9- dicarboxylate di-allyl decane-1.10- dicarboxylate di-allyl undecane-1,11- dicarboxylate di-allyl dodecane-1.12- dicarboxylate di-allyl phthalate

Merck MXM035

glycerol trithioglycollate
trimethylolpropane trithioglycollate
pentaerythritol trithioglycollate
pentaerythritol tetrathioglycollate
di-pentaerythritol hexathioglycollate
4.4'-thiobisbenzenethiol
di-allyl iso-phthalate
di-allyl terephthalte
ethane dithiol
propane dithiol
pentane dithiol

hexane dithiol

heptane dithiol
octane dithiol
nonane dithiol
decane dithiol
undecane dithiol
dodecane dithiol
ethylene glycol di-3mercaptopropionate
1.2-propylene glycol di-3mercaptopropionate
propane-1.3-diol di-3mercaptopropionate

butane-1.4-diol di-3-mercaptopropionate pentane-1.5-diol di-3-mercaptopropionate hexane-1.6-diol di-3-mercaptopropionate heptane-1.7-diol di-3-mercaptopropionate octane-1,8-diol di-3-mercaptopropionate nonane-1.9-diol di-3-mercaptopropionate decane-1,10-diol di-3-mercaptopropionate glycerol tri-3-mercaptopropionate trimethylolpropane tri-3-mercaptopropionate pentaerythritol tri-3-mercaptopropionate pentaerythritol tetra-3-mercaptopropionate di-pentaerythritol hexa-3-mercaptopropionate Also commercial polymers from Norland and Merck eg Norland 65. Norland 63 and

CLAIMS

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1. A twisted nematic liquid crystal device capable of being switched from a twisted stated to a non twisted state comprising;

two cell walls enclosing a layer of nematic liquid crystal material:

electrode structures on both walls for applying an electric field across the liquid crystal layer:

a surface alignment on both cell walls providing alignment direction to liquid crystal molecules and arranged so that a twisted nematic structure is formed across the liquid crystal layer:

means for distinguishing between the two different optical states of the liquid crystal material;

CHARACTERISED BY

- means for reducing zenithal anchoring energy in the surface alignment on one or both cell walls.
 - 2. The device of claim 1 wherein the means for reducing zenithal anchoring energy is an oligomer which is coated onto the inner surface of one or both cell walls either spread on the surface or added to the liquid crystal material.
 - 3. The device of claim 1 wherein the means for reducing and zenithal anchoring energy is an oligomer incorporated in the liquid crystal material.
- 4. The device of claim 1 wherein the means for reducing zenithal anchoring energy is N65, or MMXM035.

- 5. The device of claim 1 wherein the means for reducing zenithal anchoring energy is a material containing esters, thiols, and/or acrylate monomers.
- 6. The device of claim 1 wherein the means for reducing zenithal anchoring energy reduces the liquid crystal material order parameter at or adjacent the cell walls. 5
 - 7. The device of claim 1 wherein the means for reducing zenithal anchoring energy changes the phase of the liquid crystal material at or adjacent the cell walls.
- 8. The device of claim 1 including means for reducing azimthal anchoring energy. 10
 - 9. The device of claim 1 wherein the surface alignment provides a pretilted nematic alignment on both cell walls.
- 10. The device of claim 1 wherein the surface alignment is provided by a rubbed 15 polymer, a photo-ordered polymer or an obliquely evaporated inorganic material.
 - 11. The device of claim 1 wherein the surface alignment layer is a surface monograting with an asymmetric groove profile.
 - 12. The device of claim 1 wherein the alignment directions on the two surface are substantially perpendicular.
- 13. The device of claim 1 wherein the liquid crystal director twists by about 90° throughout the thickness of the cell. 25

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- 14. The device of claim 1 wherein the liquid crystal director twists is greater than 180 ° and less than 360°.
- 15. The device of claim 1 wherein the nematic liquid crystal material contains a small amount (<5%) of a chiral dopant material.

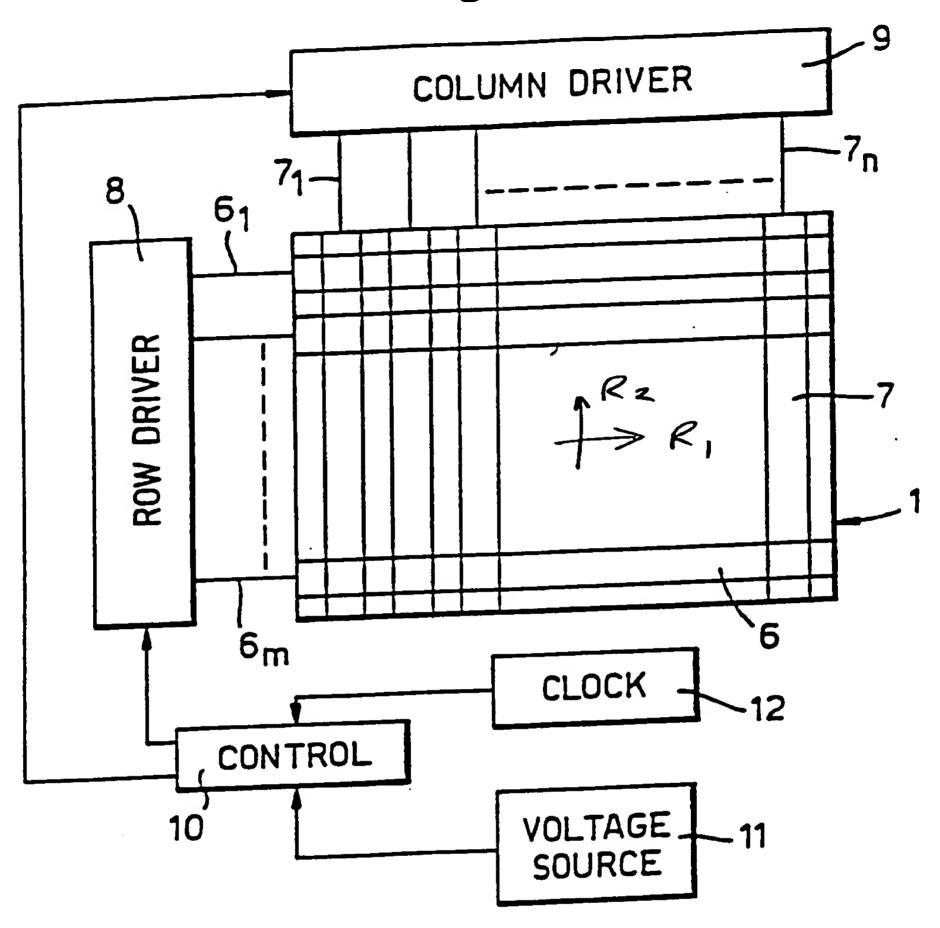
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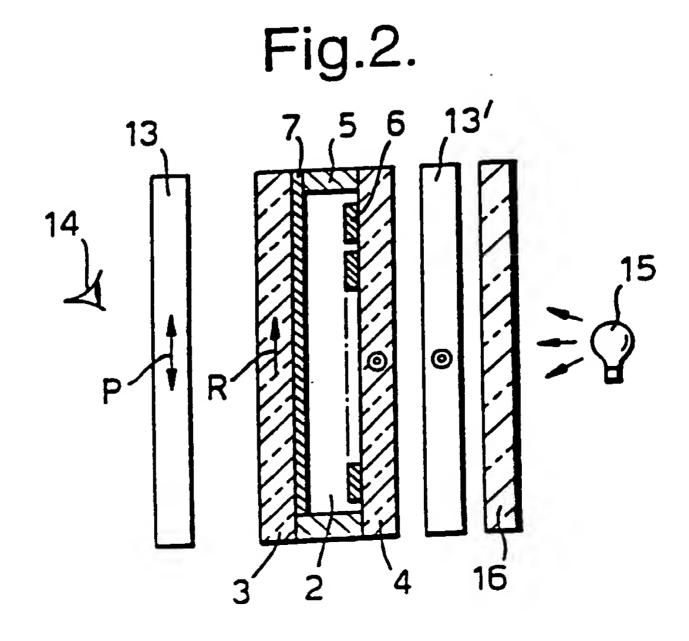
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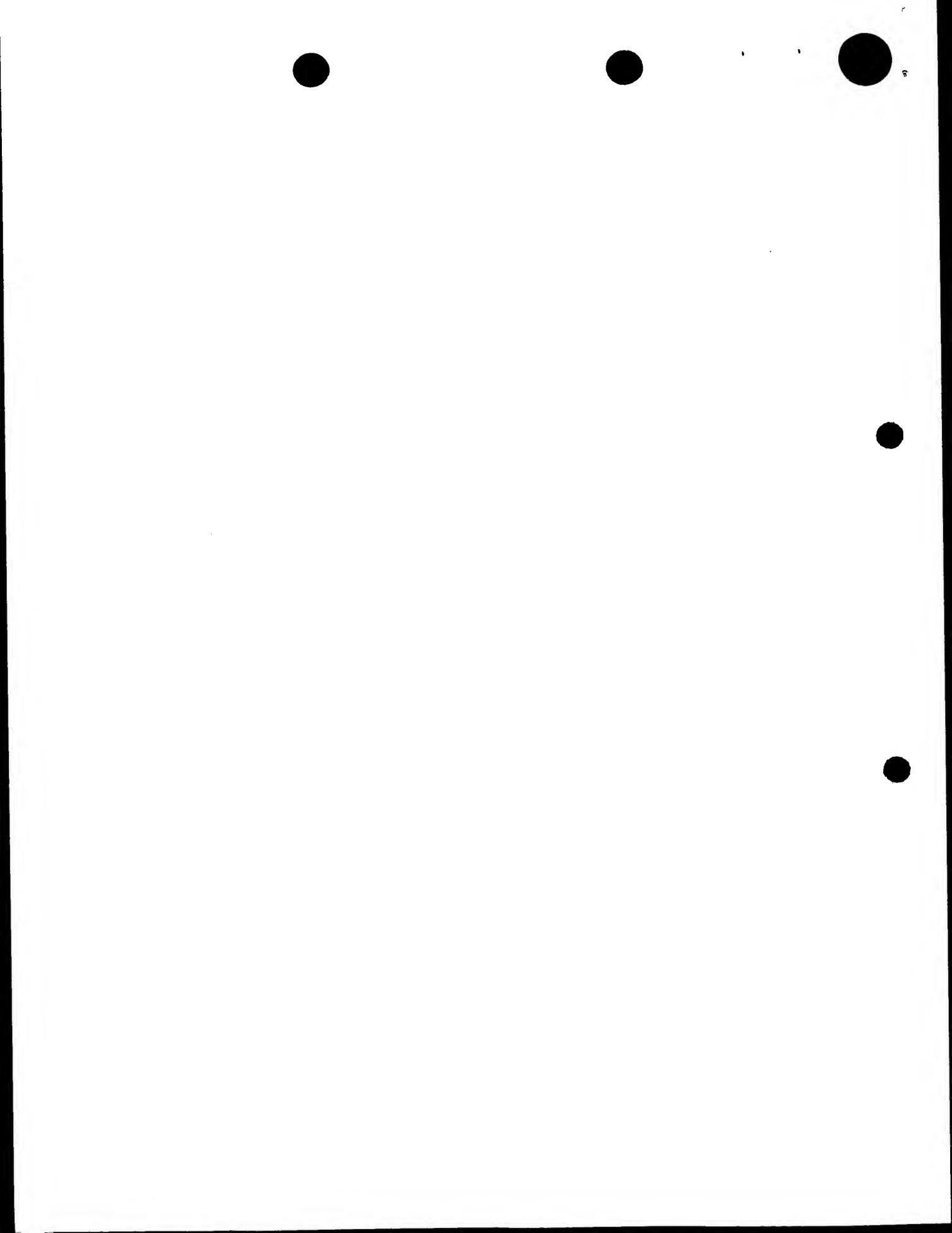
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A twisted nematic liquid crystal device has a lowered switching voltage with an enhanced contrast ratio between ON and OFF states. The improvement is provided by reducing the zenithal anchoring energy of liquid crystal molecules at a wall: additionally the azimuthal anchoring energy may also be reduced. The device comprises a cell having a layer of a nematic or long pitch cholesteric liquid crystal material contained between two walls which carry electrode structures and surface alignment treatments such as a rubbed polymer or grating structures. These alignment treatments produce a strong alignment and surface tilt to the liquid crystal molecules. The anchoring energy of such alignment and tilt may be reduced by including an amount of a treatment which is either spread on the wall or added to the liquid crystal material. The treatment may be an oligomer which may be produced by UV polymerisation of material containing esters, thiols, and/or acrylate monomers.

Fig.1.







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Figure 3

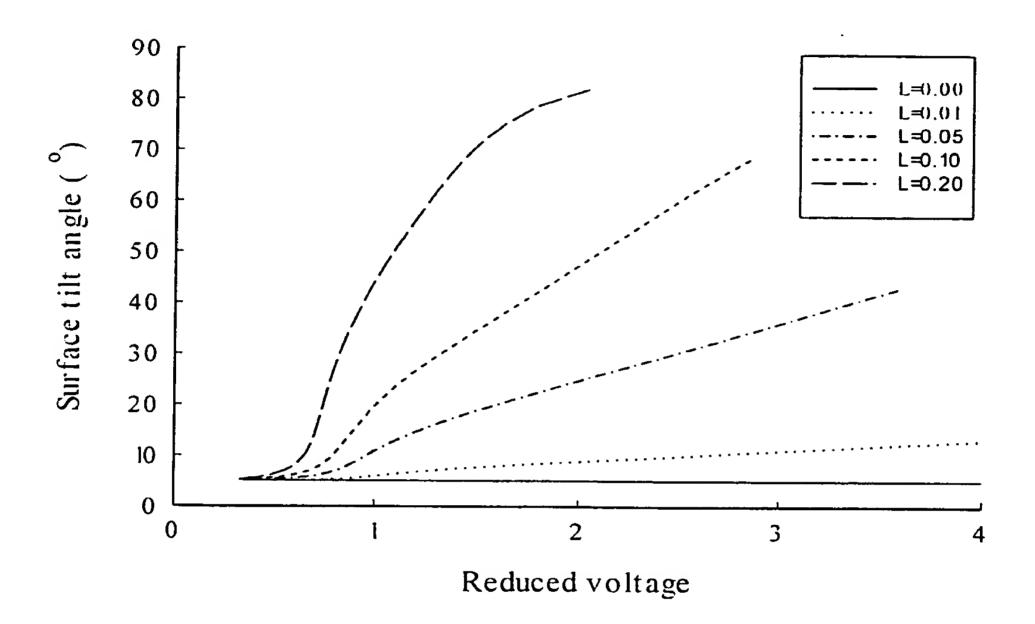
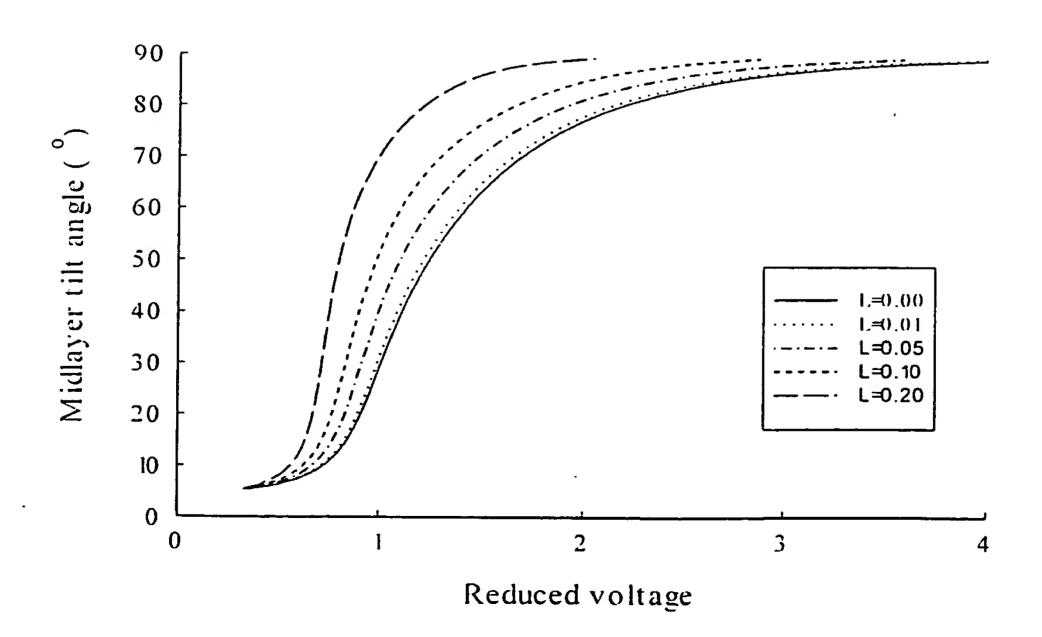


Figure 4



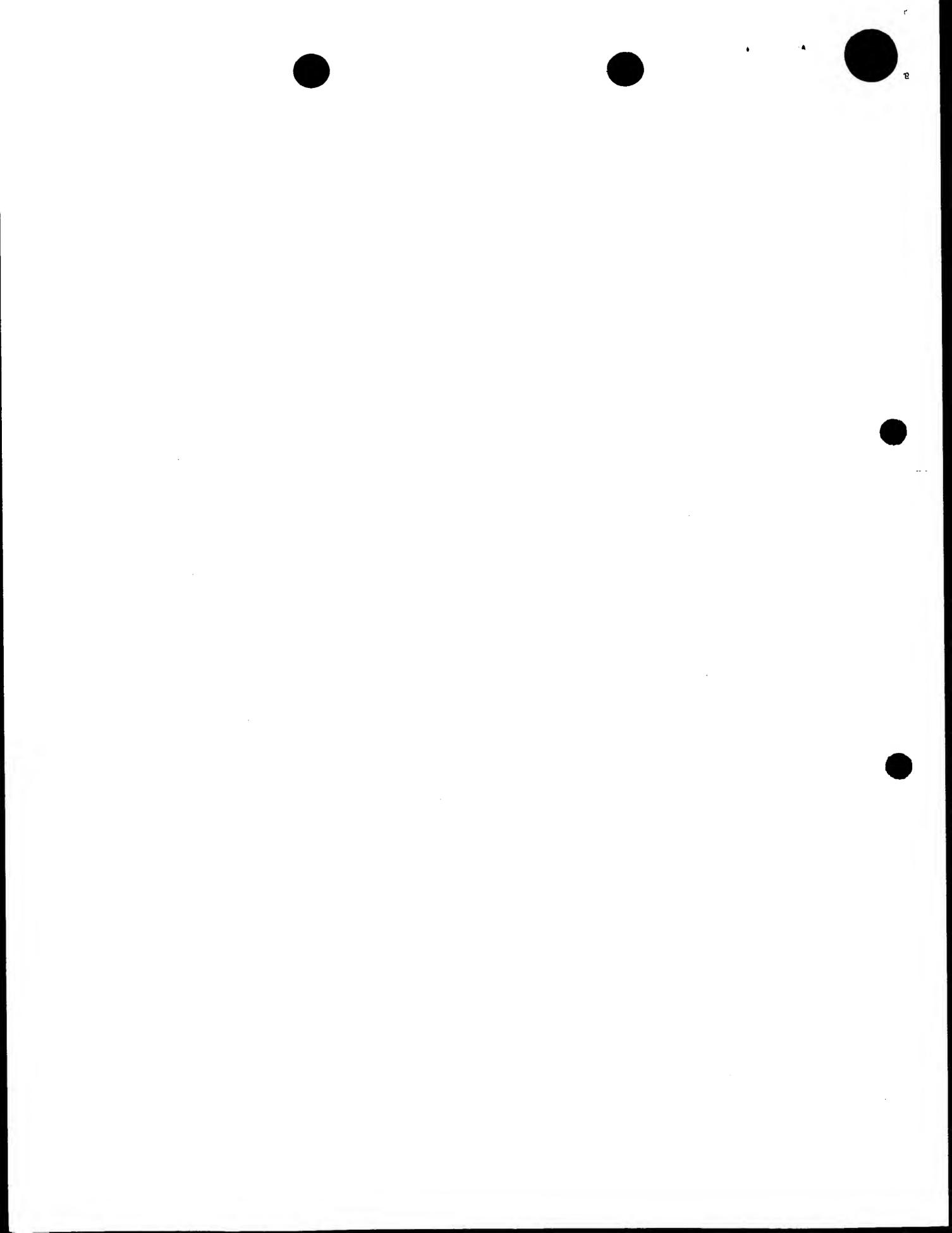
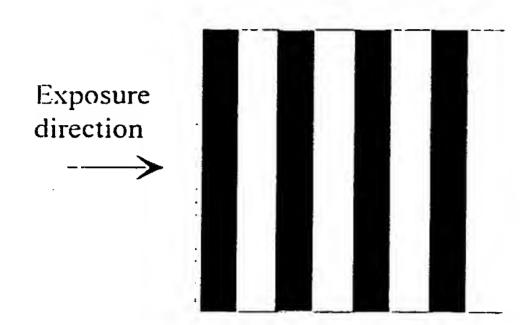


Figure 5



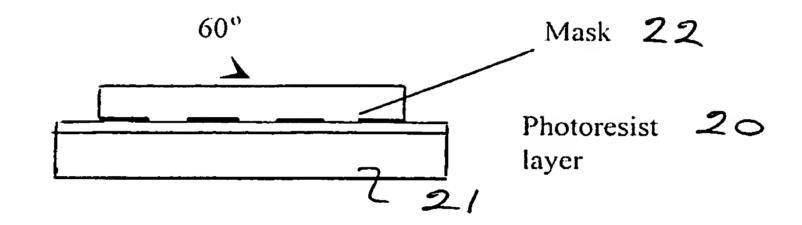
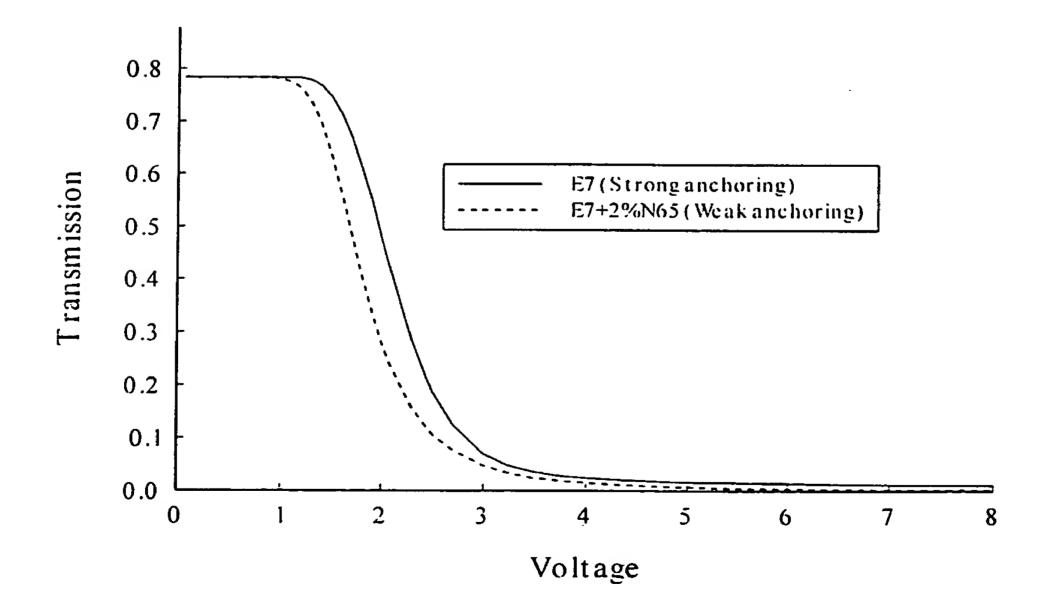


Figure 6



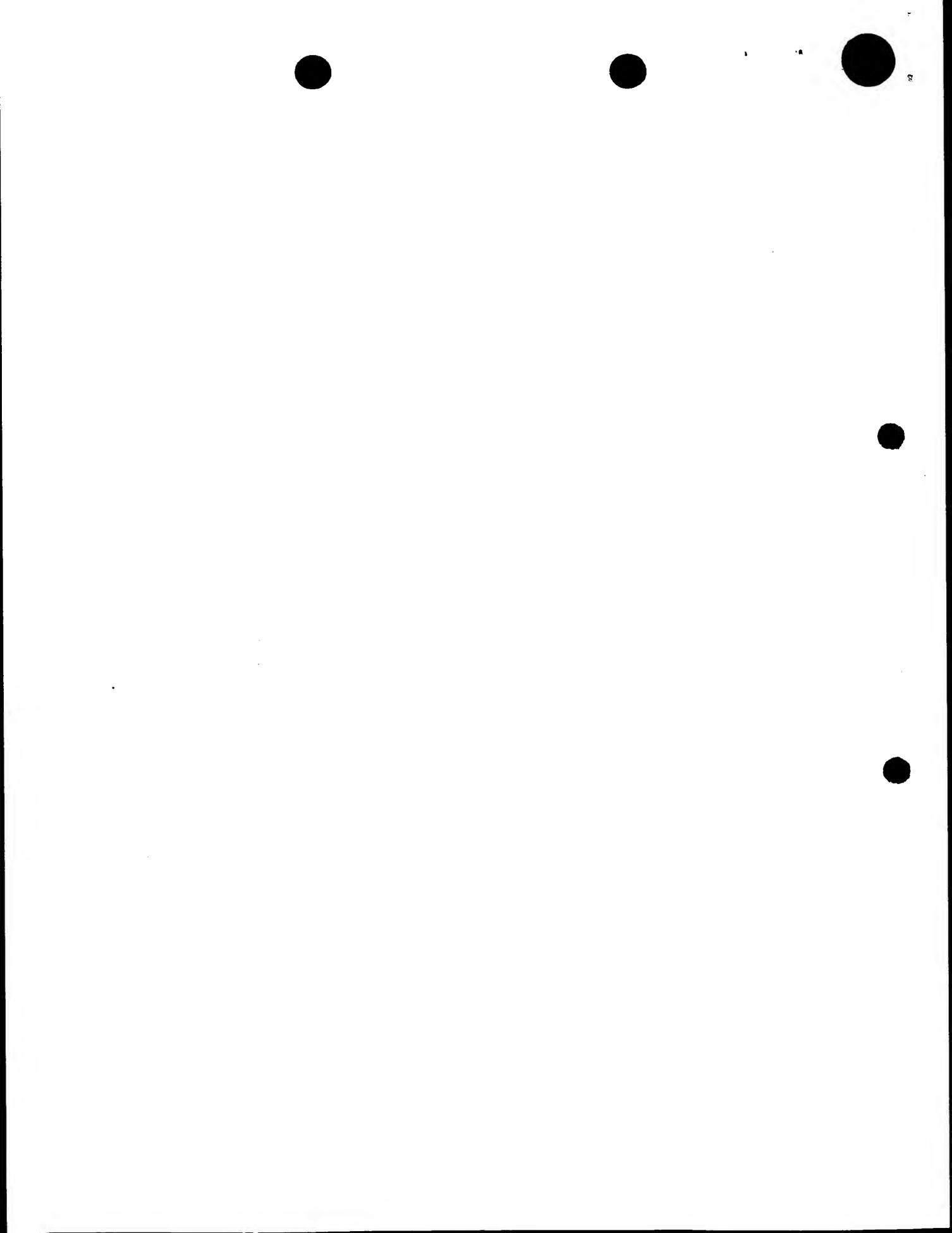


Figure 7

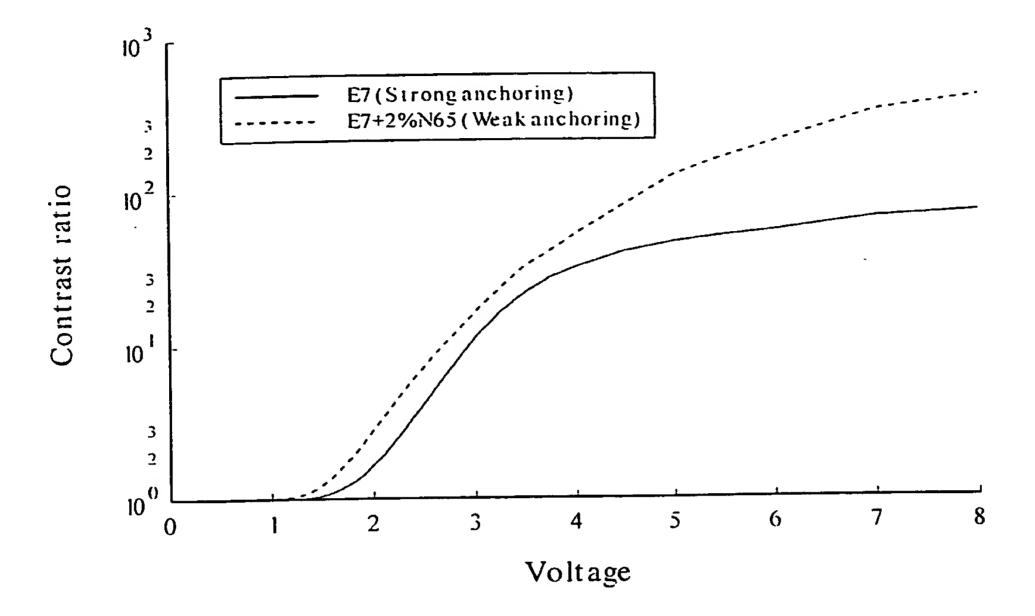
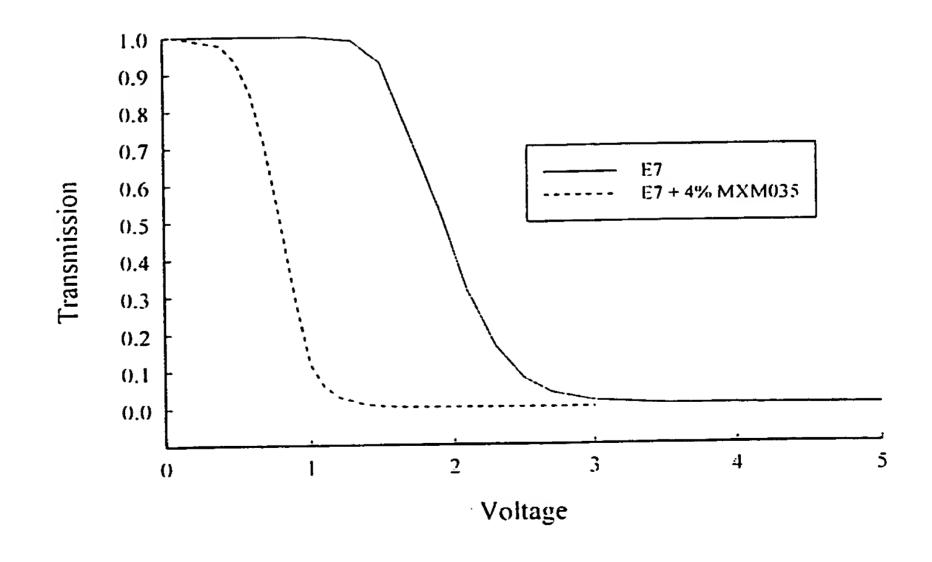


Figure 8



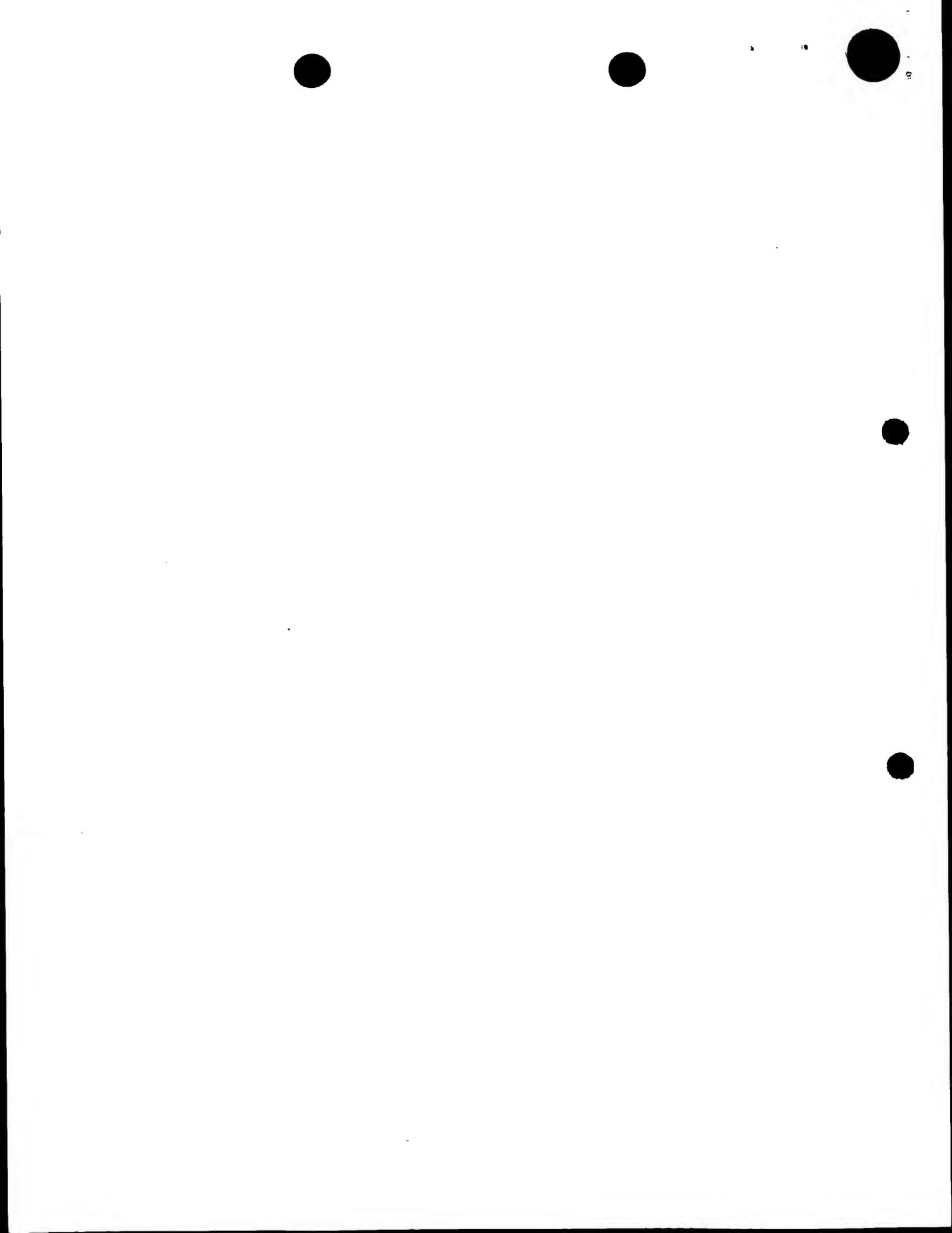


Figure 9

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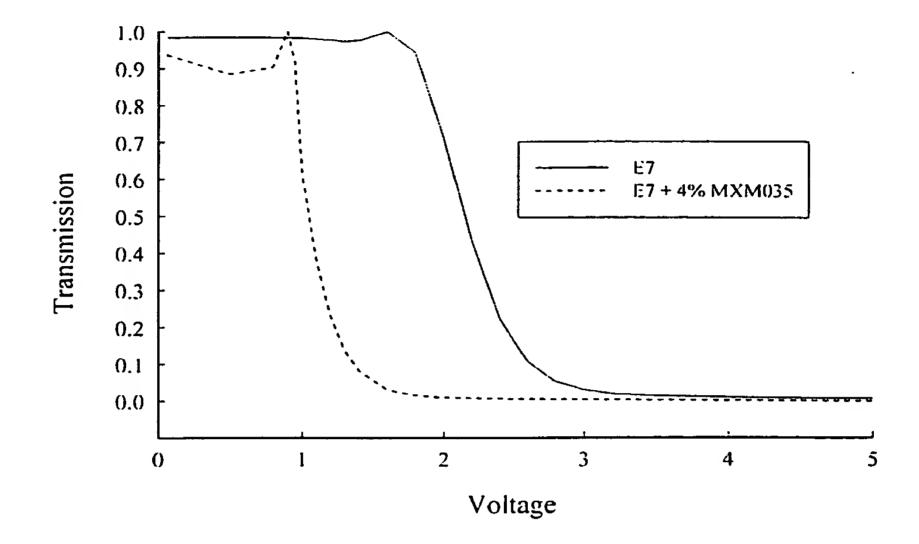
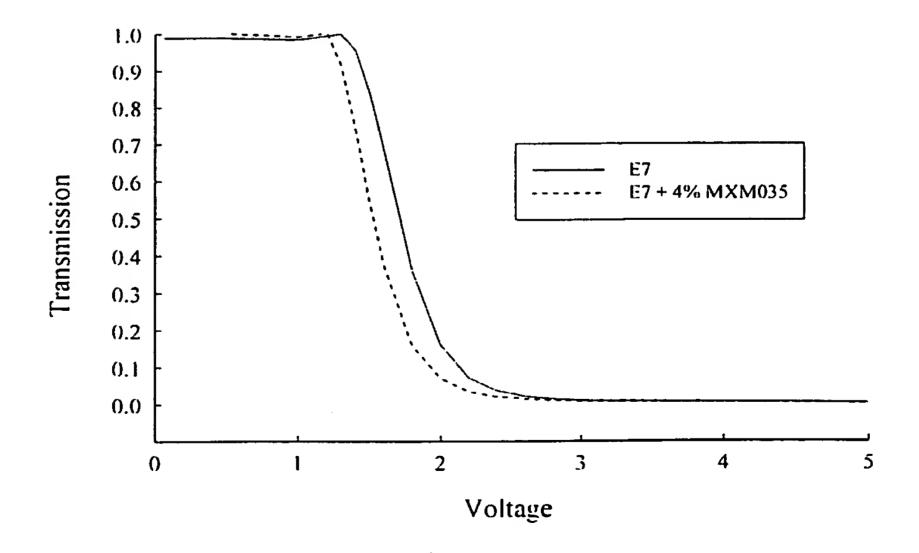
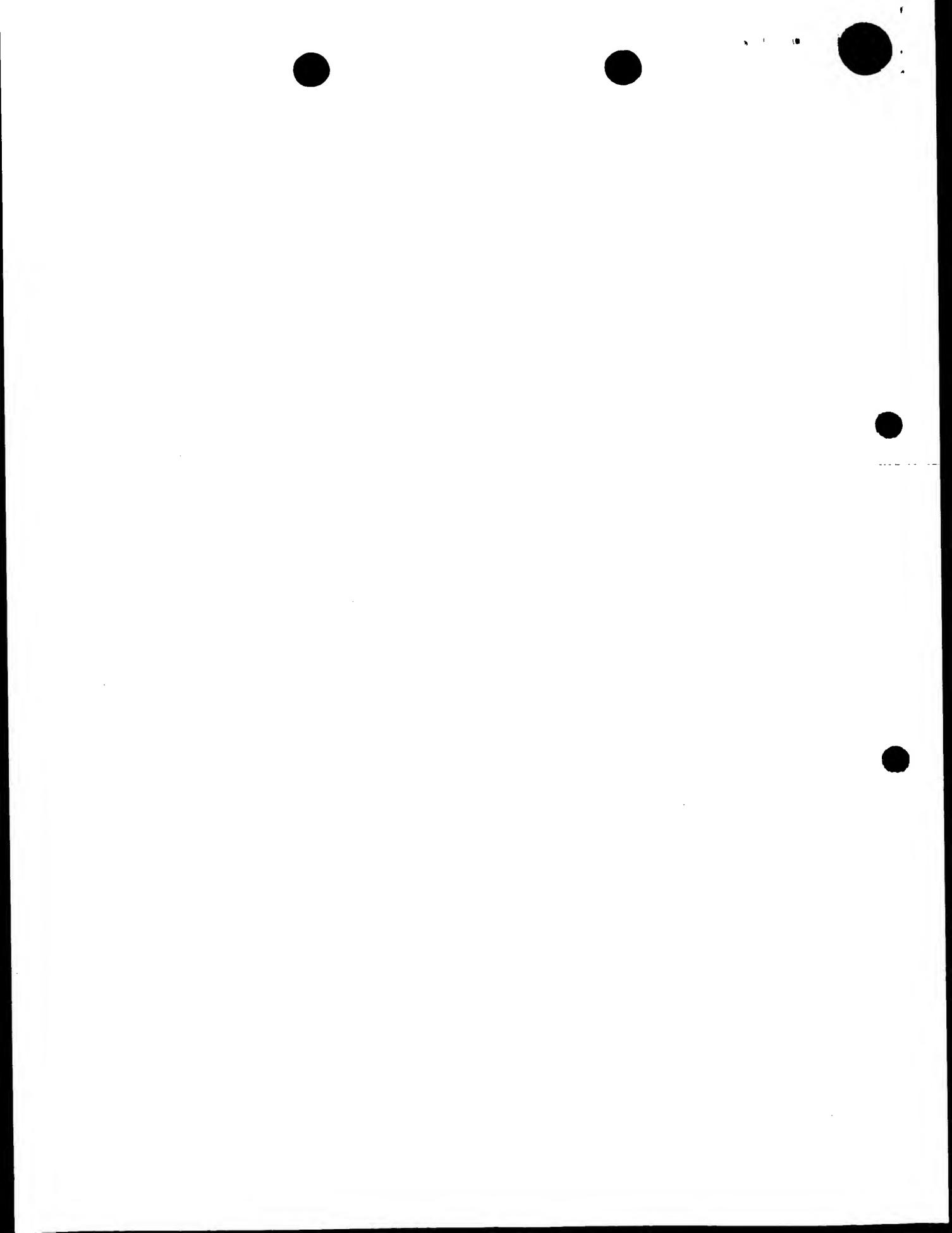


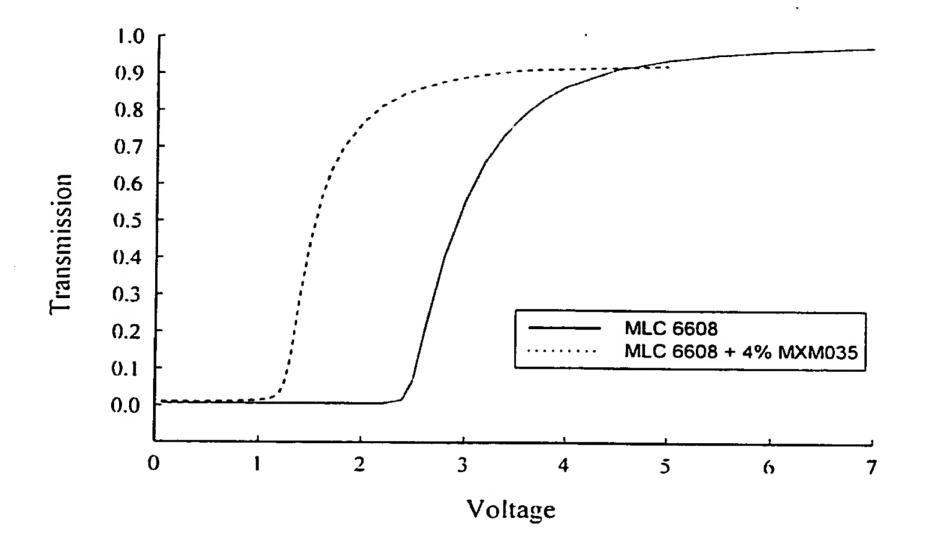
Figure 10





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Figure 11



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